ORTHOESTER COMPOSITIONS AND METHODS FOR REDUCING THE VISCOSITY OF VISCOSIFIED TREATMENT FLUIDS

Cross-Reference to Related Applications

[0001] This application is a continuation-in-part of Serial No. 10/752,752, entitled Orthoester Compositions and Methods of Use in Subterranean Applications, filed on January 7, 2004, and Serial No. 10/650,101, entitled Compositions and Methods for Reducing the Viscosity of a Fluid, filed on August 26, 2003.

Background of the Invention

[0002] The present invention relates to methods and compositions for treating subterranean well formations, and more specifically, to improved orthoester compositions comprising orthoesters and methods for reducing the viscosity of viscosified treatment fluids.

[0003] A variety of viscosified treatment fluids are used in subterranean applications, such as drilling fluids, fracturing fluids, and gravel pack fluids. Oftentimes, after the viscosified fluid has performed its desired task, it may be desirable to reduce its viscosity so that the treatment fluid can be recovered from the formation and/or particulate matter may be dropped out of the treatment fluid at a desired location within the formation. Reducing the viscosity of a viscosified treatment fluid is often referred to as "breaking" the fluid.

[0004] Well stimulation treatments, such as fracturing treatments, commonly employ viscosified treatment fluids. Fracturing generally involves pumping a viscous fracturing fluid into a subterranean formation with sufficient hydraulic pressure to create one or more cracks or "fractures." The fracturing fluid generally has a viscosity that is sufficient to suspend proppant particles and to place the proppant particles in fractures, *inter alia*, to maintain the integrity of those fractures once the hydraulic pressure is released. Once at least one fracture is created and the proppant is substantially in place, the viscosity of the fracturing fluid usually is reduced, and the fluid is recovered from the formation.

[0005] Similarly, sand control operations, such as gravel packing, use viscosified treatment fluids, often referred to as gravel pack fluids. Gravel pack fluids usually are used to suspend gravel particles for delivery to a desired area in a well bore, *e.g.*, near unconsolidated or weakly consolidated formation particulates. One common type of gravel packing operation

involves placing a gravel pack screen in the well bore and packing the annulus between the screen and the well bore with gravel of a specific size designed to prevent the passage of formation sand. When installing the gravel pack, oftentimes the gravel is carried to the formation in the form of a slurry by mixing the gravel with a transport fluid. The gravel, *inter alia*, acts to prevent the particulates from occluding the screen or migrating with the produced fluids, and the screen, *inter alia*, acts to prevent the gravel from entering the production tubing. Once the gravel pack is substantially in place, the viscosity of the gravel pack fluid often is reduced to allow it to be recovered from the well bore.

[0006] For some viscosified treatment fluids their viscosity may be related to pH. Thus, viscosity-reducing agents that reduce the pH of the treatment fluid may be added to reduce the viscosity of the fluid. Internal breakers, such as enzymes, oxidizers, acids, or temperature-activated viscosity reducers, also are used to reduce the viscosity of viscosified treatment fluids. Unfortunately, these traditional breakers may result in an incomplete or premature viscosity reduction. Premature viscosity reduction is undesirable as it may lead to, *inter alia*, the particulates settling out of the fluid in an undesirable location and/or at an undesirable time. Moreover, conventional non-delayed breakers begin to reduce the viscosity of the viscosified fluid upon addition and continue to reduce the fluid's viscosity with time until the fluid is completely broken or until the breaker is expended. Since the breaking activity begins immediately, it is common practice to start with excess viscosifier to offset the point at which the viscosity falls below an acceptable level. Using excess viscosifier is not only an added expense, it also may lead to excessive friction pressure during treatment placement.

[0007] As an alternative to using traditional breakers, breaking a viscosified treatment fluid also may be accomplished using just time and/or temperature. The viscosity of most treatment fluids will reduce naturally if given enough time and at a sufficient temperature. However, such methods generally are not practical as it is highly desirable to return the well back to production as quickly as possible as opposed to waiting for the viscosity of a treatment fluid to naturally decrease over time.

SUMMARY OF THE INVENTION

[0008] The present invention relates to methods and compositions for treating subterranean well formations, and more specifically, to improved orthoester compositions comprising orthoesters and methods for reducing the viscosity of viscosified treatment fluids.

[0009] In one embodiment, the present invention provides a method of reducing the viscosity of a viscosified treatment fluid comprising contacting the viscosified treatment fluid with an acid generated from an orthoester composition that comprises an orthoester.

[0010] In another embodiment, the present invention provides a method of reducing the pH of a viscosified treatment fluid comprising providing an orthoester composition that comprises an orthoester; contacting the viscosified treatment fluid with the orthoester composition; allowing the orthoester to generate a generated acid; and allowing the generated acid to at least partially reduce the pH of the viscosified treatment fluid.

[0011] In another embodiment, the present invention provides a method of fracturing a subterranean formation comprising contacting the subterranean formation with a fracturing fluid at a pressure sufficient to create or enhance at least one fracture in the subterranean formation; contacting the fracturing fluid with an orthoester composition comprising an orthoester; allowing the orthoester to generate a generated acid; allowing the viscosity of the fracturing fluid to decrease; and removing at least a portion of the fracturing fluid from the subterranean formation.

[0012] In another embodiment, the present invention provides a method of creating a gravel pack in a well bore comprising placing a gravel pack fluid comprising gravel particulates into a portion of the well bore so as to create a gravel pack; contacting the gravel pack fluid with an orthoester composition comprising an orthoester; allowing the orthoester to generate a generated acid; allowing the viscosity of the gravel pack fluid to decrease; and removing at least a portion of the gravel pack fluid from the subterranean formation.

[0013] In another embodiment, the present invention provides a composition comprising an orthoester that will generate an acid that is capable of at least partially reducing the viscosity of a viscosified treatment fluid.

[0014] The features and advantages of the present invention will be readily apparent to those skilled in the art upon a reading of the description of the preferred embodiments, which follows.

DESCRIPTION OF PREFERRED EMBODIMENTS

[0015] The present invention relates to methods and compositions for treating subterranean well formations, and more specifically, to improved orthoester compositions comprising orthoesters and methods for reducing the viscosity of viscosified treatment fluids. One of the desirable features of the compositions and methods of the present invention is that they provide for the delayed release of an acid and a subsequent efficient break of a viscosified treatment fluid in a desirable amount of time. The compositions and methods of the present invention are suitable for any application wherein the viscosity of a viscosified treatment fluid may be reduced by the use of an acid.

[0016] The orthoester compositions of the present invention comprise orthoesters. These orthoesters will generate acids that may reduce the viscosity of a viscosified treatment fluid. Examples of suitable orthoesters have a structure defined by the formula: RC(OR')(OR")(OR'"), wherein R', R", and R'" are not hydrogen, and R', R", and R'" may or may not be the same group. R', R", or R'" may comprise a heteroatom that may affect the solubility of the chosen orthoester in a given application. Suitable heteroatoms could include nitrogen or oxygen. Examples of suitable orthoesters and poly(orthoesters) include, but are not limited to, orthoacetates, such as trimethyl orthoacetate, triethyl orthoacetate, tripropyl orthoacetate, triisopropyl orthoacetate, and poly(orthoacetates); orthoformates, such as trimethyl orthoformate, triethyl orthoformate, tripropyl orthoformate, triisopropyl orthoformate, and poly(orthoformates); and orthopropionates, such as trimethyl orthopropionate, triethyl orthopropionate, tripropyl orthopropionate, triisopropyl orthopropionate, and poly(orthopropionates). Suitable orthoesters also may include orthoesters of polyfunctional alcohols, such as glycerin and/or ethylene glycol. Those skilled in the art with the benefit of this disclosure will recognize suitable orthoesters that may be used in a desired application. In choosing an orthoester, one should be mindful that some orthoesters have low flash points. Therefore, the choice of which particular orthoester to use should be guided by such considerations as environmental factors. The orthoester may comprise less than about 1% to about 100% of the orthoester composition.

[0017] To allow the orthoester to hydrolyze to produce an acid, a source of water is needed. The water should be present in an amount from about 2 moles of water for about every 1 mole of orthoester to an excess of water. One of ordinary skill in the art with the benefit of this

disclosure will recognize whether a suitable amount of water is present in either the orthoester composition or otherwise in the well bore for a desired application.

[0018] The orthoester compositions of the present invention also may comprise an inhibitor, which may delay the generation of the acid from the orthoester of the orthoester composition and also may neutralize the generated acid during the delay period. Suitable inhibitors include bases. Examples of some preferred inhibitors may include sodium hydroxide, potassium hydroxide, amines such as hexamethylenetetramine, sodium carbonate, and combinations thereof. In certain embodiments, a small amount of a strong base as opposed to a large amount of a relatively weak base is preferred to achieve the delayed generation of the acid and the neutralization of the generated acid for a desired delay period.

[0019] The orthoester compositions of the present invention can have any suitable form. For instance, these compositions can be used in a solution form, a gel form, or an emulsion form. In certain applications, a solution form may be useful, *e.g.*, when a faster break of a treatment fluid, is desired; in other applications, *e.g.*, when a slower break or degradation is desirable, a gel or emulsion form may be used. For the solution form, suitable exemplary solvents include propylene glycol, propylene glycol monomethyl ether, dipropylene glycol monomethyl ether, and ethylene glycol monobutyl ether. In some embodiments, mixtures of solvents and water may be beneficial, for example, to keep the orthoester solubilized. The gel form of the orthoester composition may be gelled with suitable polymers and/or surfactants. For the emulsion form, suitable emulsifiers include emulsifiers like "WS-44," which is commercially available from Halliburton Energy Services, Duncan, Oklahoma.

[0020] In the certain embodiments of the methods of the present invention, an orthoester composition of the present invention is added to a viscosified treatment fluid to reduce its pH so as to eventually at least partially reduce its viscosity. Depending on the timing required for the reduction of viscosity, the orthoester composition may provide a relatively fast break or a relatively slow break, depending on, for example, the particular orthoester chosen and the form in which the orthoester composition is provided. In some embodiments, the orthoester composition may act at a delayed rate to produce an acid that may cause a relatively controlled or delayed reduction of the viscosity of the treatment fluid. In choosing the appropriate orthoester, one should also consider the acid that will be produced in the context of the viscosified treatment fluid. Among other things, the acid should not adversely affect other

operations or components. One of ordinary skill in the art with the benefit of this disclosure will be able to select a suitable orthoester and a suitable orthoester composition to accomplish the break in a desired period of time.

[0021] Any viscosified treatment fluid that experiences a reduction in viscosity when its pH is lowered is suitable for use in the methods of the present invention. These may include, but are not limited to, aqueous gels and emulsions. Suitable aqueous gels are generally comprised of water and one or more gelling agents, while suitable emulsions are generally comprised of an aqueous phase (*e.g.*, water or a brine) and a nonaqueous phase (*e.g.*, a hydrocarbon). Viscosified treatment fluids that are suitable for use in conjunction with the orthoester compositions of the present invention may comprise a variety of gelling agents, including hydratable polymers that contain one or more functional groups such as hydroxyl, cis-hydroxyl, carboxyl, sulfate, sulfonate, amino, or amide. Polysaccharides and derivatives thereof that comprise groups such as galactose, mannose, glucoside, glucose, xylose, arabinose, fructose, glucuronic acid, or pyranosyl sulfate, may be beneficially used in conjunction with the compositions and methods of the present invention. Hydratable synthetic polymers and copolymers that contain the above-mentioned functional groups also may be used. Examples of such synthetic polymers include, but are not limited to, polyacrylate, polymethacrylate, polyacrylamide, polyvinyl alcohol, and polyvinylpyrrolidone. Copolymers of these polymers also may be suitable. The viscosifying agent used is generally combined with the water in a viscosified treatment fluid in an amount in the range of from about 0.01% to about 2% by weight of the water. The gelling agents may be crosslinked with suitable crosslinking agents that may be used to further increase the viscosity of the treatment fluid. Examples of such crosslinking agents include, but are not limited to, alkali metal borates, borax, boric acid, and compounds that are capable of releasing multivalent metal ions in aqueous solutions. Examples of suitable multivalent metal ions are chromium, zirconium, antimony, titanium, iron, zinc or aluminum. When used, the cross-linking agent is generally added to the gelled water in an amount in the range of from about 0.01% to about 5% by weight of the water.

[0022] In alternative embodiments of the methods of the present invention, an orthoester composition of the present invention may be coated or impregnated onto particulates that will be placed downhole in a subterranean treatment such as fracturing or gravel packing. When the

orthoester ultimately hydrolyzes and generates the acid, the acid may act to reduce the pH of the viscosified treatment fluid to at least partially reduce the viscosity of the treatment fluid.

[0023] Any particulate suitable for use in conjunction with subterranean applications is suitable for use as particulates in these embodiments of the methods of the present invention. For instance, natural sand, quartz sand, particulate garnet, glass, ground walnut hulls, polymeric pellets, bauxite, ceramics, or the like are all suitable. Suitable sizes range from about 4 to about 100 U.S. mesh, in certain preferred embodiments, the sizes may range from about 10 to about 70 U.S. mesh.

[0024] The orthoester compositions of the present invention may be coated onto a particulate material by any means known in the art. For instance, in one embodiment, the particulates may be coated with an orthoester composition "on-the-fly." The term "on-the-fly" is used herein to refer to an instance where one flowing stream is continuously introduced into another flowing stream so that the streams are combined and mixed while continuing to flow as a single stream as part of an ongoing treatment. Such mixing can also be described as "real-time" mixing. Batch or partial batch mixing processes may also be suitable. The coated particulate as described herein may be used as gravel particles in sand control operations, as proppant particles in fracturing operations, or as any other particulate employed in subterranean operations.

[0025] Where the orthoester composition is a relatively solid material at ambient temperatures, it may be advantageous to mix the orthoester composition with a solvent to facilitate the coating of the orthoester composition onto the particulates. A variety of solvents known in the art may be suitable. Some such solvents include, but are not limited to, acetone, propylene carbonate, dipropylene glycol methyl ether, isopropyl alcohol, or combinations thereof.

[0026] In some embodiments of the present invention, the particulates are coated with from about 0.1% to about 20% orthoester composition by weight of the particulates, more preferably from about 0.5% to about 10% orthoester composition by weight of the particulates, and most preferably, from about 1% to about 8% orthoester composition by weight of the particulate material.

[0027] In some embodiments, 100% of the particulates are coated with an orthoester composition of the present invention; in other embodiments, only a portion of the particulates may be coated. Where less than 100% of the particulates are coated with an orthoester

composition of the present invention, it may be desirable to use a higher concentration of an orthoester composition relative to that portion of the particulates to be coated. It is within the ability of one skilled in the art with the benefit of this disclosure to determine the amount of orthoester composition that will be necessary to sufficiently reduce the viscosity of a viscosified treatment fluid and to coat a portion of particulates with enough orthoester composition to achieve that goal.

[0028] Where the coated particulates are used in a sand control operation such as gravel packing, the gravel pack may be formed using any technique known in the art. In one technique, gravel particles (at least a portion of which are partially coated with an orthoester composition of the present invention) are slurried into a treatment fluid and pumped into the well bore having a filter cake deposited therein substantially adjacent to the zone of the subterranean formation that has been fitted with a gravel pack screen. In alternative embodiments, it is possible to not use a screen if desired. The gravel particulates are separated from the slurry as the delivery fluid is forced into the well bore through the screen if a screen is used. The gravel particulates are not able to flow through the mesh of the screen and are left behind, forming a gravel pack. The acid generated by the orthoester composition may then act to reduce the pH of the viscosified treatment fluid to at least partially reduce its viscosity.

[0029] In one embodiment, the present invention provides a method of reducing the viscosity of the viscosified treatment fluid comprising contacting the viscosified treatment fluid with an acid generated from an orthoester composition that comprises an orthoester.

[0030] In another embodiment, the present invention provides a method of reducing the pH of a viscosified treatment fluid comprising providing an orthoester composition that comprises an orthoester; contacting the viscosified treatment fluid with the orthoester composition; allowing the orthoester to generate a generated acid; and allowing the generated acid to at least partially reduce the pH of the viscosified treatment fluid.

[0031] In another embodiment, the present invention provides a method of fracturing a subterranean formation comprising contacting the subterranean formation with a fracturing fluid at a pressure sufficient to create or enhance at least one fracture in the subterranean formation; contacting the fracturing fluid with an orthoester composition comprising an orthoester; allowing the orthoester to generate a generated acid; allowing the viscosity of the fracturing fluid to decrease; and removing at least a portion of the fracturing fluid from the subterranean formation.

[0032] In another embodiment, the present invention provides a method of creating a gravel pack in a well bore comprising placing a gravel pack fluid comprising gravel particulates into a portion of the well bore so as to create a gravel pack; contacting the gravel pack fluid with an orthoester composition comprising an orthoester; allowing the orthoester to generate a generated acid; allowing the viscosity of the gravel pack fluid to decrease; and removing at least a portion of the gravel pack fluid from the subterranean formation.

[0033] In another embodiment, the present invention provides a composition comprising an orthoester that will generate an acid that is capable of at least partially reducing the viscosity of a viscosified treatment fluid.

[0034] Although this invention has been described in terms of some specific uses of the orthoester compositions of the present invention, the orthoester compositions may be used in other applications, for example, to degrade other acid-soluble components in a subterranean formation like the formation itself, calcium carbonate, acid-soluble components of completion equipment such as plugs, or resins (*e.g.*, thermosetting resins).

[0035] To facilitate a better understanding of the present invention, the following examples of preferred embodiments are given. In no way should the following examples be read to limit or define the scope of the invention.

EXAMPLE

[0036] While shearing in a small Waring blender, 0.48 g of guar gum was added to 91 ml of tap water. After hydrating for 20 minutes, 0.12 ml of a borate crosslinker, 0.25 ml of 25% sodium hydroxide, 1 ml of WS-44 emulsifier (available from Halliburton Energy Services, Duncan, Oklahoma), and 8 ml of tripropyl orthoformate were added in the order listed and sheared until uniformly mixed. Rheology was measured using a Brookfield PVS viscometer fitted with a B5X bob at a constant shear rate of 40 sec^{-1}. Viscosity was recorded at 5 minute intervals for the duration of the test. Representative readings are shown in the Table below. After some initial thermal thinning, the viscosity was constant until approximately 9 hours, when the sample lost viscosity rapidly. The pH at the end of the test was 4, compared to 12 when the fluid was first mixed. Once the fluid broke, the torque measurement on the rheometer was below the optimum range for accurate measurements. Although the indicated viscosity is zero, the fluid does have a finite viscosity after breaking.

Time, min.	Viscosity, cP	Temperature, °C
5	2720	76
30	2250	84
60	1370	84
120	1570	84
180	1450	84
240	1560	84
300	1270	84
360	1470	84
420	1330	84
480	1310	84
540	1560	84
555	1290	84
560	1140	84
565	1130	84
570	1020	84
575	808	84
580	625	84
585	315	84
590	0	84
595	0	84
600	0	84
605	0	84

[0037] Therefore, the present invention is well adapted to carry out the objects and attain the ends and advantages mentioned as well as those that are inherent therein. While numerous changes may be made by those skilled in the art, such changes are encompassed within the spirit and scope of this invention as defined by the appended claims.